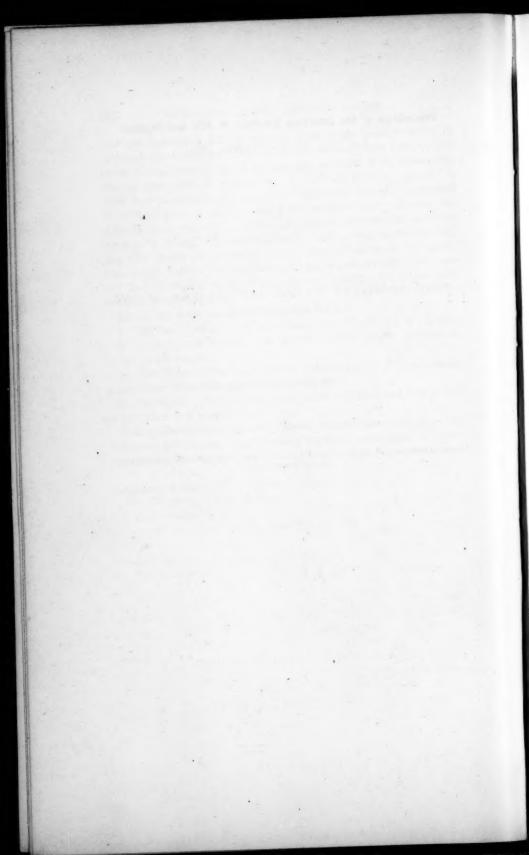
Proceedings of the American Academy of Arts and Sciences.

Vol. XL. No. 9. - OCTOBER, 1904.

SOME ADDITIONS TO THE ARC SPECTRA OF THE ALKALI METALS.

By F. A. SAUNDERS.

Investigations on Light and Heat made or published, wholly or in part, with Appropriations from the Rumpord Fund.



SOME ADDITIONS TO THE ARC SPECTRA OF THE ALKALI METALS.

By F. A. SAUNDERS.

Presented by Charles R. Cross. Received September 8, 1904.

Lenard * discovered a new series and several other lines in the arc spectrum of sodium. He removed the slit of a spectroscope and in its place focussed a real image of the arc. With suitable dispersion he observed that different parts of the arc gave different "lines," and the new ones which he discovered were emitted by the hottest vapor, near the positive pole. Konen and Hagenbach † succeeded in photographing many of these lines and finding others in the lithium spectrum which are apparently emitted under similar circumstances. The writer, also, hoped to obtain photographs of such lines, using the usual slit, if his spectrograph were designed to give very bright spectra free from astigmatism, and if an image of the proper part of the arc were cast on the slit. The attempt was made with all the elements of the lithium family and the results, which were partially successful, are given below.

The essential feature of the apparatus used was a Rowland concave grating of about 10 cm. width and 305 cm. radius, ruled with lines of somewhat unusual length on a parabolic surface. The ruled surface had an area of 5 by 8 cm. The grating was mounted with the slit close to it on a solid iron casting bolted to a brick wall. An arm, supported from this casting and constructed of heavy gas-pipe, carried the camera at its end and could be turned about a point immediately below the grating. The table carrying the grating turned with this arm. The light from the slit fell on a parabolic mirror, similar to the one on which the grating was ruled, placed at such a distance that the reflected light formed a parallel beam. This then fell upon the grating and the spectra were formed about 150 cm. from the grating along a curve which was nearly a circle of 75 cm. radius. The incident and reflected beams at the mirror made an angle of 3 degrees with one another, while the angle between the axis of the grating and the beam incident on it

^{*} Ann. der Phys., 11, 636 (1903).

[†] Phys. Zeitschr., 4, 592, 801 (1903).

varied from 12 to 21 degrees, depending on which order was being photographed. The axis of the grating was adjusted to meet the photographic film at its middle point. By rotation of the arm, this relation remained unchanged, but the focal distance changed with the angle. The camera was accordingly made adjustable along the normal to the grating, and by careful trial, three positions were obtained at which the camera could readily be set and clamped, so as to obtain spectra in good focus whose middle points lay near 3900, 5900, or 7800 tenth-meters. The whole mounting was enclosed by a wooden structure with doubly curtained door, which the observer could enter or leave during an exposure without fogging the film.

With this arrangement the spectra were almost entirely free from astigmatism for a space of 25 cm., corresponding to nearly 2700 t.-m. in the first order. Economy of light was insured by the short focus of the mounting and the large size both of grating and mirror.

The spectra were photographed on films 35 cm. long and usually 2.5 cm. wide. These were mounted in a holder which bound the film all along both edges and forced it to take such a curvature that the spectra were in focus along its whole length. This holder could be moved vertically by measurable amounts by a couple of large screws, so that several spectra could be photographed above one another on the same film. Each film took in over 3800 t.-m. at once, with good definition over almost the whole length, if the adjustments were correctly made. The scale of the photographs was nearly 11 t.-m. to the millimeter in the first order, and two sharp lines could be seen distinctly separated if they were 0.7 t.-m., or less, apart.

The films used were from the Seed Company and were coated with their 26× emulsion. A few Eastman Non-Curling films were also tried and found very satisfactory for wave-lengths less than 5900. For photographing lines in the red, the Seed films were stained with a simple cyanin bath. The writer is glad to have an opportunity of thanking Mr. R. James Wallace of the Yerkes Observatory for the formula, furnished by him, for this staining process, and recommends it to others interested, as a very simple and efficient way of sensitizing plates as far into the red as 8000 t.-m. Mr. Wallace's formula is as follows:—

Cyanin so	luti	ion	in .	Alc	oho	ol (1:	50	0)		5 cc.
Alcohol .											30 cc.
Water .											60 cc.
Ammonia											10 drops.

The plate should be bathed in this for two minutes and washed for one; it may be used at once, even before drying. Such plates do not keep for many days as a rule, though the writer has used some that were kept under very favorable conditions for a couple of months and found them still fairly good.

The source of light for the present work was usually the carbon arc, using 10 to 15 amperes, direct current. The writer is indebted to the International Acheson Graphite Co. of Niagara Falls, N. Y., for some unusually pure graphite rods with which all these spectra were taken. This graphite by itself gave only half a dozen lines (mostly Ca; no iron) outside of the band spectrum of carbon (which showed the "tails" beautifully), but when it was saturated with a salt solution, several lines of titanium came out, evidently from the graphite. These were not unwelcome, as they were always sharp, and, as their wave-lengths are given in Rowland's table of solar lines, they made excellent standards of measurement. The differences in wave-length between these lines in the sun and in the arc are too small to be worth considering in the present set of measurements. Eye observations showed that the alkali metal spectra were particularly well developed in the arc when the graphites were well saturated with salt solution and were separated by only 2 or With such a source the most successful photographs were taken; the well-known lines of the elements were then very much strengthened and broadened and the newer lines made their appearance. Fairly good photographs were, however, obtained with the arc longer, so that the "flames" were fully formed, if the light were taken from near the terminal. Exposures of three hours' duration were taken in the effort to pick up new lines in the deepest red. If the source of light could have been maintained in its most efficient condition during the whole time, the results might have been more complete, but the task of keeping the image of such lively flames as form these arcs constantly on the slit proved impossible.

A few photographs were also taken of the spark spectra of some of these elements, both with and without self-induction in the spark circuit, but no differences were detected in the relative intensities of any of the lines of the spectra of the spark or arc.

The photographs were usually taken with half the slit exposed directly to the light, and the other half covered with colored glass. In the resulting spectrum, lines in the first and second orders could easily be picked out where these overlap, as the ultra-violet lines were half the length of the others. In the deep red photographs, half the slit was

open for a short time and then covered with red glass, the other half being so covered throughout. In this way, images of unknown red lines would form part of the same spectrum with known second order lines; no shift could occur to alter their relative positions, as the colored glasses were supported independently and could be changed without affecting the position of the slit in the least. In all cases the beam of light from the condensing (quartz) lens, passing through the slit, filled the mirror and grating completely. The condensing lens was rigidly fixed throughout. The writer, for these reasons, feels certain that the photographs obtained can be relied upon to show the true positions of the lines.

The measurement of the films was accomplished by means of a Gaertner micrometer microscope with a run of 5 cm. graduated to read to 0.005 mm. Its screw was investigated and found to possess no error large enough to be worth considering. A magnifying power of about 15 diameters was used. In measuring an unknown line, in every case measurements were taken on several standard lines lying on both sides of it, and its position was calculated from each of these; 10 settings were made on each line. As a rule, the wave-length of any line, as given, is the average of several such sets of measurements taken from different photographs.

In the following tables of the complete arc spectra of the alkali elements, the writer has given in the first column the series to which the line belongs (P for principal, I for first subordinate, &c.). In the second column are placed various values for the wave-lengths, and, opposite each, in the third and fourth columns, the error as estimated by each observer and the observer's initial letter. The following are the observers quoted: L, Lehmann *; Ld, Lenard; K & R, Kayser and Runge; K & H, Konen and Hagenbach; H, Hagenbach; E & H, Exner and Haschek 1; L & D, Liveing and Dewar; B, Lecoq de Boisbaudran, and S for the writer. The custom of stating errors seems to vary with different observers. The writer believes that the errors of measurement proper are usually small compared with errors due to wrong interpretation of the photographic image. In his own experience, several settings on a diffuse line may have agreed with one another to less than 0.1 t.-m., while a different observer has made equally concordant measurements leading to a result 0.2 or more away. Where so many lines are broadened or diffuse, as in these spectra, the importance

^{*} Ann. der. Phys 5, 638 (1901). † Ann. der Phys., 9, 729 (1902). † Wellenlängen-Tabellen (1902).

of this class of error will be easily seen. The writer's own estimates of error are not based on variations in his microscope readings; if they were, they would be half or a third as large. He has tried to fix the error at such a value that the chances are extremely small that the measured wave-length will differ from the true one by more than the amount given. These estimates have been formed by the help of test measurements taken on accurately known lines, following the same method as with unknown ones.

It is usual to give an estimate of the intensity of each line along with its wave-length. This has not been done in the following tables, as such estimates have usually, especially for the greater wave-lengths, depended more on the sensitiveness of the photographic plate for each vibration than on the real intensity in the source of light. The lines of a series, of course, decrease in intensity with decrease in wave-length, those of the principal series more rapidly than the others. The first subordinate series is stronger than the second, and the new series lines are the faintest of all. Quantitative measurements of the real intensities of spectrum lines are much to be desired, but the writer does not know of any that are applicable to these spectra.

LITHIUM.

The writer was not aware until after this work was done that Konen and Hagenbach had already found the lines at 6240 and 4148, which form a new series (with 4636) in the lithium spectrum; he gives his values for the wave-lengths of these and a few other lines in the hope that they may be of value, especially as some of them differ from the values already given by considerable amounts. The line at 4148, such as it is, is visible in Figure 6, Plate 1, of Kayser's Handbuch, Vol. II, immediately to the right of 4132.44 (which by a misprint is numbered 4273 in the figure).

The "line" at 4602 deserves especial mention. Kayser* regards this as a line heavily reversed and much broadened toward the red. Hagenbach regards it as a pair of lines, the weaker one being constantly reversed, the heavier occasionally; the separation of the two amounts to over a tenth-meter. He is, apparently, ready to believe that all the lines in this spectrum are pairs with so great a separation. It is easy to obtain photographs of the strong line at 6708, and others, in which the lines are

^{*} Handbuch, 2, 366; also Plate II., Figure 5.

LITHIUM.

Series.	Wave-length.	Error.	Observer.	Series.	Wave-length.	Error.	Observer
п	(8127:34	0.27	L	I	4132.44	0.2	K & R
11	8127.0	0.3	8	II	3985.94	0.2	41
P	6708.2	0.2	K & R	ш	(3924		K & H
***	6240.8		K & H	111	8921.8		E & H
Ш	6240.3	0.4	S	I	3915.2	0.2	K & R
I	6103.77	0.03	K&R	II	3838.3	3.0	**
II	4972.11	0.1	41	1	3794.9	5.0	- 66
	4636.14		н	I	3718.9	5.0	44
ш	4636.04		K & H	I	3670.6	5.0	61
	4636.3	0.4	8	P	3232.77	0.03	er
	(4602.37	0.1	K & R	P	2741.39	0.03	**
	4603.04)	0.01	н	P	2562.60	0.03	44
1	4602.00		н	P	2475.13	0.1	**
	4603.2	0.2	S	P	2425.55	0.1	* "
	4601.6	0.2	s	P	2394.54	0.2	66
II	4273.44	0.2	K&R	P	2373.9		L & D
ш	(4149.1		К& Н	P	2359.4		**
111	4148.2	1.0	s				

sharp enough to show a doubling, if the components were even closer than a tenth-meter, and no such doubling has been observed. The curious reversals obtained by Hagenbach certainly call for an explanation, but it is difficult to adopt the one given by him in view of the absence of doubling in those lines where it would be most easily detected. The writer took a set of six photographs of the 4602 group on a film, using the second order spectrum (5.5 t.-m. to the mm.) and varying the exposures and amounts of vapor in the arc so as to furnish wide differences among the set. In these photographs the points of maximum density in the image on either side of the "reversal" remain in constant

positions, even though the amount of vapor in the arc is small, in which case they are separated from each other by an absolutely clear space on the negative. The conclusion seems unavoidable from these images that we have here to deal with no reversal at all, but with two lines; a strong one at 4603.2, much broadened towards the red, and a weaker one at 4601.6, broadened toward the violet, neither of them being ordinarily reversed. If this view be adopted, the spectrum of lithium shows another analogy to that of sodium, for, in the latter spectrum, immediately beside the pair in the first subordinate series which is homologous to Li 4602 lies a faint pair broadened toward the violet in a similar manner.

The 4602 group presents the same aspect in the spark spectrum as in the arc.

SODIUM.

In the spectrum of sodium, the new series of Lenard has been successfully photographed and measured; a new term in the red has been added and a faint haze at 4372 was detected on one photograph which is doubtless the sixth member of the series. The pair at 4472 was so diffuse that the lines could not be seen separately; the setting was made on the middle of it. The writer's measurements differ considerably from those of Lehmann and of Konen and Hagenbach on several lines; a repetition of the measurements led to the same values. Konen and Hagenbach give a line at 4973 which does not appear with certainty on any of the present photographs; nor does there seem to be any companion to 4660. The pair at 7410 is exceedingly faint, and may possibly not belong to sodium. It has, however, approximately the same separation as the Lenard series pair near by, and, like that pair, the line of greater wave-length is slightly the stronger. If this is a member of another series, it would seem likely that the other lines are too faint to have been observed, unless, possibly, it could be grouped with the pair at 5670 and the lines at 4975 and 4660. An extremely faint group was observed at 8210, but it was impossible to determine just what it was; this was the greatest wave-length which was photographed on these films.

The lines 5100, 4820, and 4730 mentioned by Lenard could not be found on the photographs, nor were eye observations with a plane grating any more successful.

It may be worth noting that the wave-number differences for Lenard's series (III) are as follows: 14.72, 14.77, 18.2, and 18.7. As the first

SODIUM.

Series.	Wave-length.	Error.	Observer.	Series.	Wave-length.	Error.	Observer
	(8194.76	0.2	L'		4820		Ld
I	8196.1	0.4	s	п	4752.19	0.15	K&R
	(8184.33	0.2	L	II	4748.36	0.15	61
I	8184.5	0.4	s		4730		Ld
	7418.3	0.4	s	I	4669.4	0.5	K&R
	7410.0	0.4	S	I	4665.2	0.5	41
III	7377.4	0.4	S		 4660		K & II
III	7869.4	0.4	8		4660.2	0.5	s
II	6161.15	0.1	K&R	ш	4633.1		K & H
II	6154.62	0.1	**	111	4629.5	1.0	s
P	5896.16		•		14629.4		K & H
P	5890.19			III	4625.5	1.0	S
I	5688.26	0.15	"	II	4546.03	0.2	K&R
1	5682.90	0.15	**	II	4542.75	0.2	41
	5675.92	0.15	46	I	4500.0	1.0	4
	5670.40	0.15	66	I	4494.3	1.0	66
	5531.7		K & H	777	(4470		Ld
III	5582 7	0.4	8	III	44725	2.0	S
***	5527.1		K & H	II	4423.7		L & D
Ш	5528.2	0.4	S	II	4420.2		66
11	5153.72	0.1	K&R	I	4393.7		**
11	5149.19	0.1	44	1	4390.7		**
	5100		Ld	III	4372	5.0	S
1	4983.53	0.2	K&R	II	4343.7		L & D
1	4979.30	0.2	es	1	4325.7		46
	∫4976.1		K & H	P	8803.07	0 03	K & R
	4975.0	0.4	8	P	3302.47	0.03	" "
	4973.0		K & H	P	2852.91	0.05	**
***	(4918.5		K & H	P	2680.46	0.1	**
III	4918.4	1.0	s	P	2593.98	0.1	- 4
***	(4910.1		K & H	P	2543.85	0.1	м
Ш	4914.0	1.0	8	P	2512.23	0.2	"

POTASSIUM.

Series.	Wave-length.	Error.	Observer.	Series.	Wave-length.	Error.	Observer
	7931.8	0.5	s		(4863.8		L&D
	(7699.3	5.0	K&R	II	4864.5	0.8	S
P	7697		R		4862		R
P	7701.92	0.52	L		4856.8		L & D
	7699.08	0.3	S	I	4856.8	0.8	S
	7665.6	5.0	K & R		4857		R
P	7664		R	II	(4850.8		L & D
P	7668.54	0.52	L	11	1 4851.0	0.8	S
	7664.91	0.3	S		4829		R
I	6966.3	0.4	S		4808.8		L & D
	6938.8	0.5	K & R	ı	ý 4803.8		44
II	6939		R	1	4803		R
	6939.5	0.4	S	II	4801		R
	6911.2	0.5	K & R		(4796.8	***	L & D
II	6913		R		14798		R
	6911.8	0.4	S		4788.8		L & D
1	5832 23	0.05	K & R		4767		R
1	5812.54	0.05	**	1	4759.8		L & D
II	5802.01	0.05	44	1	4760		. R
II	5782.67	0.05	"		4642.35	0.3	R
1	5359.88	0.15	**		4642.5	0.3	S
1	5343.35	0.15	"		4638.6		R
II	5340 08	0.15	**	P	4047.86	0.03	K & R
II	5323.55	0.15	**	P	4044.29	0 03	**
1	5112.68	0.2	" .	P	3447.49	0.03	"
II	5099.64	0.2	66	P	3446.49	0.03	**
1	5097.75	0.2	**	P	3217.76	0.03	"
II	5084.49	0.2	ee	P	3217.27	0.03	**
1	4965.5	1.0	44	P	3102.37	0.1	"
II	4956.8	1.0	11	P	3102.15	0.1	**
I	4952.2	1.0	et	P	3034.94	0.1	"
II	4943.1	1.0	et '	P	2992.33	0.15	44
	4870.8		L & D	P	2963.36	0.2	44
I	4871.3	0.8	S	P	2942.8	1.0	"
	4870		R		* ,		

two of these are probably accurate to one part in 80, while the two last are much less accurate, it seems fair to say that these differences are probably much smaller than the value for the usual series (17.2).

Many unsuccessful attempts have been made to find a simple formula which would express Lenard's series. The formulae of Kayser and Runge, Rydberg, Fowler and Shaw,* and Ritz,† and modifications of these, have been tried. Unless the formula contained four adjustable constants, it could not be made to fit the observations with any degree of precision. As almost any series, if not too accurately known, could be represented by a four-constant formula, no results of this work are given.

In the spectrum of potassium, two new lines were found, one in almost the position predicted for it. 1 It is one of the hitherto missing first pair of the first subordinate series, which is, for some obscure reason, very faint. (Ritz has given reasons for believing this to be the first rather than the second subordinate series, as Kayser and Runge classified it.) The other member of this pair was not found, owing to the broadening of the line at 6939, near which it doubtless lies. The other new line (7931.8) was so faint that its companion, if it is a member of a pair, could not be seen. The first term of the principal series was excellently photographed on several films and the writer feels considerable confidence in the value of the wave-lengths given for these lines. They are recorded to the second place of decimals, as the difference between the values could be determined more accurately than the values themselves. The best measurements were taken on photographs where the potassium was present as an impurity and the lines were fine and sharp, though measurements on heavily reversed images of these lines gave concordant results.

The line at 4642 seems to be outside the series formation, and, along with the faintness of the first subordinate pair, offers a very odd peculiarity in this spectrum.

RUBIDIUM.

Three new lines were found in the spectrum of rubidium. One is a line at 3158 (not seen as a pair) belonging to the principal series; another, a very diffuse and faint line at 5171, which, with 5234, forms a pair in the second subordinate series. The third is a line at 7759.5, which is a companion to the first subordinate series line 7757.9. The

Astrophys. J., 18, 21 (1903).
 † Ann. der Phys., 12, 264 (1903).
 † See Ritz, Ann. der Phys., 12, 264 (1903).

RUBIDIUM.

Series.	Wave-length.	Error.	Observer.	Series.	Wave-length.	Error.	Observer
	8513.26	0.26	L		(5259.8		В
	(7950.46	0.32	L	I	5260.51		R
P	7947.6	0.5	S		5260.5	0.4	S
	(7805.98	0.54	L		5234.6		R
P	7799		R	II	5234.0	0.7	S
	7800.2	0.5	S		(5194.8		В
atell.	7759.5	0.5	S	I	5195.76		R
	(7753.58	0.54	L		5195.9	0.5	S
I	7757.9	0.5	S		5165.35		R
	(7626.66	0.32	L	II	5171	2.0	S
I	7619.2	0.3	S		5161.8		В
-	(7406.19	0.25	L	I	5 5151.20		R
II	17408.5	0.4	S	1	1 5150.8	0.5	S
	(7277.01	0.25	L	II	5 5132		R
II	7280.3	0.3	S	11	5133.5	0.8	S
	6306,8		R		5085.8		В
	(6298.7	0.2	K & R	I	5089.5		R
I	6298.8	0.3	S		5088.6	0.6	S
	(6206.7	0.2	K&R	I	5076.3		R
I	6206.7	0.3	S	1	1 5075.7	0.6	S
	(6159.8	0.2	K&R	1	5037		R
II	6160.0	0.3	8	I	5021.8		В
	6071.2	0.2	K & R	1	1 5023		R
II	6071.1	0.3	· S	I	5017		R
I	5724.41	0.15	K & R	I	4983		R
II	5654.22	0.15	"	11	4967		R
I	5648.18	0.15	"	P	4215.72	0.03	K & R
**	5579.3		R	P	4201.98	0.03	44
II	1 5579.4	0.4	S	P	3591.74	0.05	**
	5 5431.83	0.15	K & R	P	3587.23	0.05	**
I	5431.9	0.4	S	P	3351.03	0.05	"
**	5 5391.3		R	P	3348.86	0.05	"
II	5391.2	0.4	S	P	3229.26		R
	5 5362.94	0.2	K&R	P	3228.17		R
I	5363.1	0.4	S	P	3158.7	0.8	S
**	5 5322.83		R	-		1944	
II	5323.1	0.5	S				

CAESIUM.

Series.	Wave-length.	Error.	Observer,	Series.	Wave-length.	Error.	Observer.
I	9211.86	0.7	L		6217.6		R
IV?	9171.88	0.7	L	satell.	6217.6	0.3	S
P	8949.92	0.76	L		6213.4	0.5	K & R
I	8766.10	0.32	L	I	6213.1	0.3	S
P	8527.72	0.32	L		6034.43		R
Ш	8080.02	0.48	L	II -	6034.8	0.3	S
	(8019.62	0.48	L	I	6010.59		R
III	8007.1	0.5	S	satell.	5847.86		R
II	7944.7	0.3	S	I	5845.31		R
	(7616.58	0.44	L	II	5839.33		\mathbf{R}
II	7609.7	0.3	8	II	5746.37		R
IV	7280.5	1.0	S	I	5664.14		R
	(7227.46	0.44	L	I	5635.44		R
IV	7228.8	1.0	S	11	5574.4		R
	6984		R	II	5568.9		R
satell.	6983.8	0.3	S	I	5503.1		R
	6973.9	5.0	K&R	I	5466.1		R
I	6973.1	0.8	S	I	5414.4		R
	6869		R	II	5407.5		R
III	6872.6	1.0	8	I	5351		R
	6829		R	I	5341.15		R
III	6826.9	1.0	S	I	5304		R
	6723.6	5.0	K & R	I	5256.96		R
1	6723.7	0.2	S		- 5209		R
	(6630		R	I	5199		R
IV	6630.5	1.0	S	I	5154		R
IV	6588.0	1.0	S	P	4593.34	0.05	K & R
••	6590		R	P	4555.44	0.05	£ 44
II	6587.8	0.8	S.	P	3888.83	0.1	41
***	6472		R	P	3876.73	0.1	"
Ш	6475	2.0	8	P	3617.08	0.3	44
***	(6438		R	P	3611.84	0.2	"
III	6434	2.0	S	P	8477.25		R
IV	6359	3.0	S	P	3398.40		R
	(6354		R	P	3348.72		R
11	6855.3	0.3	S	P	3314		R
IV	6325	3.0	8	P	3287		R

results of the measurements in the deep red differ from those of Lehmann to a marked degree. As a check on the present methods, the writer took a set of measurements of several other and better known lines in this spectrum. The results, which are included in the table, agree reasonably well with those of Kayser and Runge. As a further check, the wavenumber differences for the pairs were calculated, using the writer's values for the wave-lengths. The results were:—

P series.	Sub. series I.	Sub. series II.
237.8	234.7	237.7
	235.6	237.7
	235.8	237.1
	236.2	237.3
	236.3	232.8
	233.5	

The constancy of these numbers is satisfactory, with the exception of the short wave-length ends of the series, where the measurements do not pretend to be accurate. A similar table calculated from Lehmann's results shows a much wider divergence.

Ramage has noted a line at 6306; nothing was seen at this place except a ghost of the strong line at 6299. He has also given a sharp line at 5165; at this point on the writer's photographs appeared a sharp line which was the head of a carbon band.

CAESIUM.

In the caesium spectrum, five new lines were found. The one at 7944.7 was predicted by Ritz and is a member of the second subordinate series, along with 7609.7.

Two new series can be arranged from the odd lines in this spectrum, which might be called the third and fourth subordinate series, as they evidently belong to this class.

III.	IV.
8080	?
8019	9171 ?
6872.6	7280.5
6826.9	7228.8
6475	6630.5
6434	6588.0
	6359
	6325

The wave-number differences of these pairs are approximately constant: they are: 96, 97.5, 97.7, 98.5, 98.4, and 80. The last pair, being on the verge of invisibility, is very inaccurately measured. These differences are much less than for the usual series, being about 0.177 as much. The line of greater wave-length in the pairs has slightly greater intensity. All the lines in these series are so exceedingly diffuse that their positions cannot be measured with much accuracy; it did not seem worth while on this account to attempt to fit a formula to them. From an inspection of their positions, it seems likely that they are not so directly connected with the first and second subordinate series as in the case of Lenard's series in the sodium spectrum. They appear to run together to a common end, which lies somewhat nearer the red than the end of the other series. It seems most unlikely from their appearance that they can be due to any impurity, as in that case they might fairly be expected to be sharp when faint; they are, however, always diffuse. These series are faint, and of approximately equal intensity.

It does not appear to have been previously noticed that the heavier line of each pair in the first subordinate series is accompanied by a satellite (lines all observed by Ramage) on the red side, forming a "secondary" series, using Rydberg's term. The writer has calculated the wave-number differences of the pairs in the caesium spectrum, using Lehmann's data for the two extreme pairs and his own for most of the rest. The results are as follows:

P series.	Sub. series I.	Sub. series II.
553.2	552.0	554.1
	531.9	554.2
	542.3	553.7
	547.2	554.6
	549.7	

It will be noticed that the values for the first subordinate series are lower than the others, and have an evident drift, with the exception of the first, which is possibly in error. As the first member of each pair is accompanied by a satellite (none have yet been observed for the first and last lines), the wave-number differences were calculated between the satellite and the line of shorter wave-length. The result is as follows:

Wave-number differences.

Calculated from main line.

Calculated from satellite.

 531.9
 553.7

 542.3
 553.9

 547.2
 554.7

It will be seen at once that the differences calculated from the satellites agree beautifully with those of the second subordinate series. parently, then, the wave-number difference for the first subordinate series, as usually calculated, should vary slightly, increasing with decreasing wave-length. A glance at the table of differences for rubidium shows the same effect in that spectrum also, and there, too, if we use the satellite at 7759.5 (the only one yet observed) with the line 7619.2, we obtain a difference of 237.3 instead of 234.7, thus bringing this value into agreement with those for the second subordinate series. This principle may be used to calculate the positions of the other satellites in the rubidium spectrum. They should be at 9213.6 (using Lehmann's line 8766.10 for the calculation), 6299.6, and 5725.1, thus being within very short distances of their parent lines. As the latter are broadened toward the greater wave-lengths they cover up the satellites, so that these have not yet been observed. The satellites in the spectra of lithium, sodium, and potassium are also, probably, too close to their parent lines to be distinguishable.

The writer wishes to express his indebtedness to the committee in charge of the Rumford Fund for a grant covering the expenses of this investigation.

Syracuse University, June, 1904.